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entanglement density polymers preferentially form non-fibrillated DZ's; crazes when formed are more resistant to craze breakdown in these polymers. A comprehensive model of these entanglement effects have been developed which explains the natural extension ratios of crazes and DZ's, the craze to DZ transition and the craze fibril stability.

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PROPERTIES OF CRAZES AND DEFORMATION ZONES IN GLASSY POLYMERS

by

Edward J. Kramer

FINAL REPORT

U.S. ARMY RESEARCH OFFICE

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ABSTRACT

New experimental methods, holographic interferometry and quantitative transmission electron microscopy, have been developed to investigate the microstructure, mechanical properties and failure of crazes and deformation zones DZ's in glassy polymers. Plasticization by the environment is found to be the major factor in environmental crazing and cracking. Air crazing, and the transition to more ductile DZ behavior, is controlled largely by the entanglement density of the polymer glass. Low entanglement density polymer craze readily and the craze fibrils break down rapidly to form cracks. High entanglement density polymers preferentially form non-fibrillated DZ's; crazes when formed are more resistant to craze breakdown in these polymers. A comprehensive model of these entanglement effects has been developed which explain the natural extension ratios of crazes and DZ's, the craze to DZ transition and the craze fibril stability.

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SCIENTIFIC BACKGROUND

INTRODUCTION

Soon after the introduction of glassy transparent thermoplastics it was observed that these materials often developed dense arrays of what appeared to be surface cracks at tensile stresses below those required to cause fracture. In many liquid environments in fact this phenomenon can occur at very low stresses, indeed residual stresses from molding operations are often sufficient. Crazing, as this came to be known from its obvious resemblance to the crazing phenomena in ceramic glazes, is now recognized to be an important possible response of all glassy polymers, both amorphous and semicrystalline, to tensile stress.

Central to most of the current interest in this phenomenon was the discovery⁽¹⁾ that the craze in glassy polymers, unlike its namesake in ceramics, is capable of bearing a load; it is not a true crack. Although the craze is not a crack, there is massive evidence that crack initiation in these materials occurs primarily by a process of craze breakdown^{2,3}. If surface crazing can be suppressed, certain polymers, such as polymethylmethacrylate (PMMA) which is ordinarily brittle at room temperature, become ductile⁽⁴⁾, because the craze breakdown process for crack initiation is no longer possible. On the other hand the fact that a craze (or group of crazes) is invariably generated at the tip of a propagating crack results in a fracture toughness, as measured in standard fracture mechanical experiments, far in excess of the true work to create two undeformed crack surfaces. In polymers which are glassy at room temperature, crazing at the crack tip is the primary source of plane strain fracture toughness.

The development of tougher rigid plastics will almost certainly require better control of the crazing response. To achieve this control better

fundamental understanding of both craze structure and properties, as well as the kinetics of the nucleation and growth of crazes, will be necessary. Although there has been considerable research on the structure of air crazes (some of which will be reviewed in the next section), there has been little work on the structure of environmental (solvent) crazes. Even less work has been done on the mechanical properties of either type of craze and almost none on trying to relate observed craze structure to these properties. Yet is the mechanical properties of the craze that are the prime determinants of the fracture response, both crack nucleation and propagation. Moreover the crazing kinetics also depend to some extent on these properties.

The paucity of information on the craze structure/mechanical properties relationships in part reflects the fact that determining these properties has been difficult, if not impossible, until this work began.

SUMMARY OF IMPORTANT ACCOMPLISHMENTS AND FINDINGS

The development of major new tools for investigating crazing and shear deformation in glassy polymers was a major accomplishment under these grants. The first tool was holographic interferometry which enabled the first quantitative measurements of the displacement, strain and stress distributions along long solvent crazes to be made. Several major findings followed rapidly on the heels of this development.

1) The first demonstration that plasticization of craze fibrils by the environment affects the mechanical properties and microstructure of environmental crazes. This work led to a deeper understanding of why some environments are "stress-crazing" environments while some are "stress-cracking", i.e. produce a very weak craze.

2) The first direct measurements of the strain energy release rates of growing crazes which demonstrated that current theoretical models of solvent craze growth criteria were incorrect.

These experiments culminated in a review article which is widely regarded as the premier review of environmental cracking and crazing⁵.

The second tool was quantitative transmission electron microscopy which allowed all the measurements that could be made on a coarse scale with holographic interferometry to be made on a much finer scale. In the course of this work it was necessary to develop novel methods of preparing and straining uniform thin films of glassy polymers as well as methods of quantitatively analyzing TEM craze images to obtain truly local values of craze surface displacements, craze surface stresses and craze fibril extension ratios and volume fractions. The new methods had sufficient resolution to be applied to air crazes, as well as solvent crazes. These developments, in turn, produced dramatic increases in our knowledge of crazing including the following major findings:

- 1) The microscopic mechanism by which air crazes widen was shown to be surface drawing rather than fibril creep. Craze fibrillar matter is produced by drawing from a thin "active zone" (~5 μ m thick) at the craze-bulk interface. The drawing produces fibrils of a constant "natural" extension ratio ER, much as the drawing of a textile fiber does.
- 2) The craze tip was shown to advance by a fluid-like instability of strain softened polymer (the Taylor meniscus instability) that produces finger-like growth rather than requiring void nucleation ahead of the craze tip. Most of the craze fibril structure is produced by surface drawing behind the tip.
- 3) Air crazes were shown to be strongly load bearing with only a small stress concentration at their tip. This finding rules out a negative pressure induced plasticization as a primary mechanism of craze growth.
- 4) An important transition in craze microstructure and mechanics with film thickness was discovered. As film thickness decreases the plastic constraint on the strain softened zone at the craze tip weakens and craze growth by the

meniscus instability mechanism is no longer possible. The "craze" in these thin films is more like a perforated sheet and accounts for a number of artifact observations of anomalous craze microstructure in the literature.

5. Certain polymers like polycarbonate were found to be resistant to crazing in thin films and formed plane stress deformation zones (DZ's) instead. The mechanism of DZ growth was also shown to be surface drawing but the production of fine fibrillar material did not occur.

With these findings as a basis we begin to look for systematic behavior from one polymer to the next. The thin film techniques proved to be very convenient for surveying a large number of different homopolymers, copolymers and even polymer blends such as polystyrene polyphenylene oxide. The results of this survey were revolutionary.

1) The first major discovery was that the natural ER of crazes was highly correlated with the entanglement density of the polymer. Polymers with a high density of entanglements (ED) had a low ER and vice versa.

2) Craze surface stress measurements in these crazes increased with increasing ED. At a high enough ED ($ED > 5 \times 10^{26}$ strands/m³) polymers formed DZ's in preference to crazing. In such high ED polymer films highly ductile behavior was observed.

3) The ER in DZ's also correlated strongly with the ED of the polymer but $(ER)_{DZ} < (ER)_{CRAZE}$ in the same polymer.

These experimental insights into the importance of molecular entanglements for craze microstructure and resistance to crazing rapidly led to progress on the theoretical side. Models of the craze fibril formation process were developed in which the formation of the fibril surface requires destruction of strands in the entanglement network either by chain scission (low T, high molecular weight M and high strain rates) or disentanglement (high T, low M and low strain rates.)

Evidence for chain scission comes from crazing in highly crosslinked polymers as well as "staining" of broken chain ends. The higher ER of crazes is due to the lower final ED of the fibrils after strands are lost due to fibril surface creation.

Evidence for chain disentanglement at higher T's (but well below T_g) is now strong. Although craze ED's are constant with T for high M polymer at high strain rates, they increase markedly with T at low strain rates. Lower M polymers show the increase beginning at lower T's. The strain rate, required to maintain a certain ED as M is increased, decreases as $M^{-2.6 \pm 0.6}$. This dependence is roughly that expected for chain disentanglement by the reptation mechanism.

These ideas had important implications for craze fibril stability but before these could be checked, a new test, called the fragility test, had to be developed. This test allows one to quantitatively measure craze fibril breakdown and its statistics. These were found to follow a Weibull distribution in strain. Using this distribution one can predict the dependence of craze breakdown on sample size. Crazes were always observed to break down in the active zone, where more polymer is being drawn into the craze fibrils. Although the critical strain for crazing is not dependent on M, the median strain for craze fibril breakdown is strongly M-dependent. In polystyrene this strain increases from the critical crazing strain ($\sim 0.7\%$) at $M=50,000$ to over 15% at $M=2 \times 10^7$.

The quantitative exploration of these phenomena required much better techniques for quantifying craze microstructure, particularly the craze fibril diameter and spacing. For this purpose small single X-ray (SAXS) and electron (SAES) scattering were developed. SAES has proved to be an extremely efficient method in that both images and diffraction patterns from the same craze can be obtained nearly simultaneously.

These tools were applied to a study of a diluted entanglement network polymer, polystyrene PS diluted with low M PS too small to entangle. Again the critical strain for crazing was independent of dilution. The median strain for craze fibril breakdown decreased rapidly with increasing low M diluent and approached the crazing strain at a high M volume fraction of 0.3.

Various models were explored to correlate the data on the monodisperse and diluted polymers. It was found that the fibril stability correlated well with n_e , the number of effective entangled strands in each fibril which survive the fibrillation process. For monodisperse polymers this number decreases due to the presence of chain ends. For the diluted polymers it decreases with dilution due to the fact that the end-to-end distance of a strand becomes larger than the fibril diameter thus markedly decreasing the strand survival probability. Craze fibril stability increases exponentially with n_e . A model that rationalizes this dependence on a statistical basis has been proposed by us.

Environmental crazing was not neglected in recent years. An excellent model system was developed in which the activity of the environment (CO_2 gas) in the polymer (PS) could be controlled simply by controlling the gas pressure at high pressures. The result is the CO_2 first acts as a strong plasticizer as the pressure is increased but then T_g of the polymer increases as the change in polymer free volume with pressure becomes important. Quantitative TEM investigation of crazes produced in this environment demonstrated conclusively that plasticization is the most important factor in environmental crazing.

Surface energy effects can however become important if enough network strands have to be broken. We have found that in plasticizing environment (eg. $\text{C}_2\text{Cl}_3\text{F}_3$ in PS) we can increase the critical strain for crazing from <0.15% to >0.8% by crosslinking. At high crosslink densities we observe a new phenomenon, environmental DZ's. Apparently the local increase in mobility of the polymer

molecules associated with the deformation is enough to increase markedly the diffusion coefficient of the solvent in the glass with the result that it can penetrate and plasticize the active zone of the DZ. The critical strains for forming DZ's in the crosslinked PS in the environment are considerably lower than those required to form such DZ's in air and the boundaries of the DZ's are sharper. These results will be prepared for publication shortly.

It is especially gratifying to note that this research on crazing and deformation of polymer glasses lead this year to the award of the High Polymer Physics Prize of the American Physical Society (donated by Ford Motor Co.) to Professor E.J. Kramer, jointly with Dr. R.P. Kambour of General Electric. The citation reads, "for pioneering and outstanding contributions to the understanding of crazing in polymers".

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